

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/KR04/003530

International filing date: 30 December 2004 (30.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 60/533,225  
Filing date: 31 December 2003 (31.12.2003)

Date of receipt at the International Bureau: 01 March 2005 (01.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
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PCT/KR 2004/003530  
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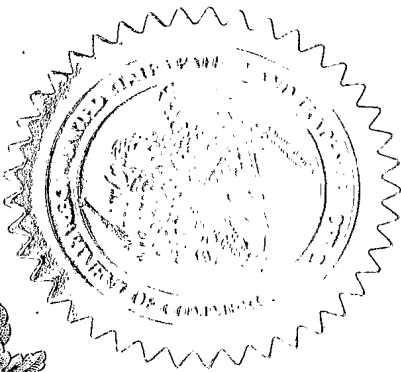
**APPLICATION NUMBER: 60/533,225**

**FILING DATE: December 31, 2003**

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53 (c).

<b>Filing Date</b>		December 31, 2003		<b>Docket No.</b>		2859-0120P	
<b>INVENTOR(S)/APPLICANT(S)</b>							
<b>Given Name (first and middle (if any))</b>		<b>Last Name</b>		<b>RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)</b>			
Jens Martin		PAULSEN		Ngatea, New Zealand			
<input type="checkbox"/> Additional inventors are being named on the separately numbered sheets attached hereto							
<b>TITLE OF THE INVENTION (280 characters max)</b>							
CATHODE POWDER WITH SIZE DEPENDENT COMPOSITION AND METHOD TO PREPARE THE SAME							
<b>CORRESPONDENCE ADDRESS</b>							
Birch, Stewart, Kolasch & Birch, LLP or Customer No. 02292 P.O. Box 747 Falls Church							
<b>STATE</b>	VA	<b>ZIP CODE</b>	22040-0747	<b>COUNTRY</b>	U.S.A.		
<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>							
<input checked="" type="checkbox"/> Specification		Number of Pages: <u>Eighteen (18)</u>		<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76.			
<input checked="" type="checkbox"/> Drawing(s)		Number of Sheets: <u>Three (3)</u>		<input type="checkbox"/> Other (specify): _____			
<b>METHOD OF PAYMENT (check one)</b>						<b>PROVISIONAL FILING FEE</b>	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. <input checked="" type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees. <input type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number 02-2448, if necessary.						<input type="checkbox"/> Small Entity (\$80.00) <input checked="" type="checkbox"/> Large Entity (\$160.00)	

22581 U.S. PTO  
60/533225

123103

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

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2859-0120P

(Rev. 09/30/03)

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## **Cathode powder with size dependent composition and method to prepare the same**

### **Technical field**

This invention relates to a powdery material, used as active cathode material in  
5 rechargeable lithium batteries. It also relates to devices using the cathode material and to a process to prepare the said cathode material.

### **Summary of invention**

This invention disclosed a general approach to improve properties of powdery  
10 materials, used in electrodes for rechargeable batteries; it also disclosed non-uniform powdery electrode materials. The general approach is the principle of non-uniformity. The application of this approach allows to prepare non-uniform electrode materials. Contrary to non-uniform materials, conventional uniform materials do not allow for a full optimization. The non-uniform approach relates composition of particles of the powder, where the  
15 composition varies with the size of the particles. In a preferred implementation of this invention, the non-uniform approach also relates to single particles of the powder. Such particles have a composition, which differs in the inner and outer bulk and surface. The non-uniform approach may relate not only to composition but also to further parameters like morphology.

20 In a preferred implementation of this invention small particles have an averaged composition with a lower cobalt content than larger particles. In a further preferred implementation of this invention, the inner bulk of the particles has a composition near to  $\text{LiCoO}_2$ . The outer bulk is a lithium manganese nickel cobalt oxide.

Disclosed is also a method to prepare said powdery materials at low cost. The  
25 method involves a co precipitation reaction using seeds. The seed particles have a non-narrow size distribution. After the reaction a precipitate covers the seed particles. The precipitation reaction is characterized that the seed particles have a significantly different transition metal composition than the precipitate. The precipitation reaction is furthermore characterized that

the precipitate forms a layer of uniform thickness, covering the seed particles.

### Background of invention

State of art batteries apply uniform cathode materials. The (averaged) composition of small and large particles is the same. Uniform materials also have a similar composition in the inner and outer bulk of a single particle.

LiCoO<sub>2</sub>, charged to 4.4V or higher voltage is the superior material regarding reversible capacity, gravimetric and especially volumetric energy. Unfortunately, LiCoO<sub>2</sub> charged to  $\geq 4.4V$  shows high capacity fading, low safety, and, in contact with the electrolyte reactivity (electrolyte oxidation) is observed.

Commercial rechargeable lithium batteries almost exclusively apply LiCoO<sub>2</sub> as cathode. LiCoO<sub>2</sub> delivers 137 mAh/g reversible capacity if charged to 4.2V. Charged to 4.3V it delivers approx. 155 mAh/g, at 4.4V approx. 170 mAh/g and at 4.5V it delivers approx. 185 mAh/g. An increase of charging voltage to 4.4 or 4.5V could drastically increase the energy density of batteries compared with the standard 4.2V charging. Unfortunately, unprotected LiCoO<sub>2</sub> cannot be cycled at  $> 4.3V$  because of poor capacity retention and poor safety properties

Coating of LiCoO<sub>2</sub> particles has been suggested to protect the surface from unwanted reactions between electrolyte and the charged (=delithiated) Li<sub>x</sub>CoO<sub>2</sub>. The coating approach is for example described by Y. J. Kim et al., J. Electrochem. Soc. 149 A1337, J. Cho et al., J. Electrochem. Soc. 149 A127, J. Cho et al., J. Electrochem. Soc. 149 A288, Z. Chen et al., J. Electrochem. Soc. 149 A1604, Z. Chen, J. Dahn, Electrochem. and solid-state letters, 5, A213 (2002), Z. Chen, J. Dahn, Electrochem. and solid-state letters, 6, A221 (2003), J. Cho et al., Electrochem. and solid-state letters, 2, 607 (1999), J. Cho and G. Kim, Electrochem. and solid-state letters, 2, 253 (1999), J. Cho et al., J. Electrochem. Soc. 148 A1110 (2001), J. Cho et al., Electrochem. and solid-state letters, 3, 362, (2000), J. Cho et al., Electrochem. and solid-state letters, 4, A159, (2001), Z. Whang et al., J. Electrochem. Soc. 149, A466 (2002), J. Cho, Solid State Ionics, 160 (2003) 241-245.

Coating can to some degree improve certain properties like fading and safety, it is however not clear if this is caused by the coating layer. In Z. Chen, J. Dahn, Electrochem. and solid-state letters, 6, A221 (2003) as well as in Z. Chen, J. Dahn, Abs 329, 204<sup>th</sup> ECS Meeting, Orlando it was shown that a similar treatment (wash+heat) without applying a coating layer  
5 causes the same improvement of cycling stability. The improvement however is temporary and vanishes after storage of the cathode.

Different mechanisms cause the fading of materials like  $\text{LiCoO}_2$ . A first is the precipitation of reaction products of decomposed electrolyte onto the surface of  $\text{LiCoO}_2$  forming resistive surface layers. A second is the chemical decomposition of  $\text{LiCoO}_2$  in the  
10 presence of electrolyte, thereby the outer bulk changes chemically and structurally. A third is the degradation of bulk  $\text{LiCoO}_2$  occurring in the absence of electrolyte, this degradation can be a crystal structural degradation (for example transformation to spinel) or a morphological gradation (electrochemical grinding, causing loss of electrical contact of crystallites). The first and second mechanism can be prevented or reduced by coating. The third requires a  
15 modification of the bulk.

Similar as the capacity fading, also safety problems are caused by different mechanism. First, delithiated  $\text{LiCoO}_2$  tends to oxidize electrolyte, which is a strong exothermic reaction. If the local temperature is high enough, the electrolyte oxidation becomes fast, more heat evolves and the battery might go to thermal runaway. Secondly, delithiated  $\text{LiCoO}_2$  in the  
20 bulk itself is unstable and might collapse towards denser phases, releasing modest amounts of heat, the reaction not involves electrolyte. The first mechanism can be prevented or reduced by coating. The second requires a modification of the bulk.

In most cases the coating accounted for less than 2-5% of the weight of the cathode. The stoichiometry of the total cathode is only marginally changed, coated materials are  
25 basically uniform materials, because the composition of large and small particles is similar, and the composition of inner and outer bulk is basically the same. The actual invention discloses non-uniform materials, where the composition changes significantly. Contrary to coating, the "non-uniform approach" relates to the whole bulk or at least to large parts of the

outer bulk. It allows for a principally different and much more radical optimization.

The described coating approaches have not fully solved the stability problem at  $> 4.3V$ .

Particularly unsolved problems are one or more of :

- 5 - non complete coating of surface. Example: A wetting of the cathode powder with a gel or solution followed by a drying typically does not result in a completely covered surface.
- not enough adhesion between coating layer and cathode. During electrode processing and during cycling (change of crystallographic unit cell volume of  $LiCoO_2$  as function of state of charge) significant strain occurs. The strain causes a peel-off of the coating layers, leaving large areas unprotected. This problem is especially pronounced if the coating layer and the  
10 cathode do not form a solid state solution.
- Chemical incapability : After coating usually a heating step is applied. During the heating the coating layer might decompose the cathode. Example : Coating  $LiCoO_2$  with lithium manganese spinel is difficult or impossible because the spinel and  $LiCoO_2$  contacting each other decompose forming cobalt oxide and  $Li_2MnO_3$ .
- 15 - Conduction problems : Insulators (as  $Al_2O_3$ ,  $ZrO_2$  ...) are suggested for the coating layers. A particle, fully covered by an insulator, is electrochemically inactive. If the surface is fully covered, then the layer has to be extremely thin (to allow "tunneling" of electrons). It is questionable if such thin layers can be achieved and if they will prevent the electrolyte-surface reactions.
- 20 - Coated layers are too thin to improve the safety
- Sharp two phase boundaries : If the  $LiCoO_2$  and the coating layer do not have a solid state solution, then lattice strains are localized at the boundary, which reduces the mechanical stability. A braking of particles during extended cycling is possible.

Complex cathode materials with layer structure have been disclosed. Some show a  
25 better cycling stability than  $LiCoO_2$  if cycled at  $> 4.3V$ , they also show better safety. Typical examples are layered cathode materials being solid state solutions within the ternary system  $LiMn_{1/2}Ni_{1/2}O_2 - LiNiO_2 - Li[Li_{1/3}Mn_{2/3}]O_2 \leftrightarrow LiCoO_2$ . In this patent application we will use abbreviation for the stoichiometry "NMO" where "N" is the Mn, "M" is the Ni and "O" is the

cobalt composition. Some examples are :

"110" -  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  or  $\text{Li}[\text{Li}_x(\text{Mn}_{1/2}\text{Ni}_{1/2})_{1-x}]\text{O}_2$ ,  $x \geq 0$ ,  $|x| < 1$  (Dahn et al. in Solid State Ionics 57 (1992) 311, or T. Ohzuku, Y. Makimura, 2001 ECS meeting (fall), Abstr. 167)

"442" -  $\text{LiMO}_2$  or  $\text{Li}[\text{Li}_x\text{M}_{1-x}]\text{O}_2$   $\text{M}=(\text{Mn}_{1/2}\text{Ni}_{1/2})_{1-y}\text{Co}_y$ ,  $x \geq 0$ ,  $|x| < 1$ ,  $y=0.2$

5 (Paulsen&Ammundsen, 11th International Meeting on Lithium Batteries (IMLB 11), Cathodes II, Ilion/Pacific Lithium)

"111" -  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  (Makimura&Ohzuku, Proceedings of the 41<sup>st</sup> battery symposium on 2D20 and 2D21, Nagoya, Japan 2000 or N. Yabuuchi, T. Ohzuku, J. of Power sources 2003, (in print)

10 "118" -  $\text{LiCo}_{0.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$  (S. Jouanneau et al., J. Electrochem. Soc. 150, A1299, 2003)

"530"  $\text{Li}[\text{Li}_{1/9}\text{Mn}_{5/9}\text{Ni}_{1/3}]\text{O}_2$ , "530mod"  $\text{Li}[\text{Li}_{1/9}\text{Mn}_{5/9}\text{Ni}_{1/3}]\text{O}_{1.75}$  (J. Dahn, Z. Lu, US patent application 2003/0108793A1, Z. Lu et al., J. Electrochem. Soc. 149 (6) A778 (2002))

Despite of some improvements these materials are not truly competitive. Remaining problems are one or more of:

15 - High cost : "118" for example has raw materials cost similar as  $\text{LiCoO}_2$ , however, compared to  $\text{LiCoO}_2$  which can be prepared by cheap routes (solid state reaction) the cost of preparation (typically involving mixed precursors like mixed hydroxides) is much higher.

- Low volumetric energy density: Low cobalt materials like "110" or "552" have low Li diffusion constant. To obtain a sufficient rate performance, powders consisting of particles  
20 with smaller crystallites and some porosity of particles are required. The obtained porosity of electrodes is too high. Additionally, the crystallographic density is significantly smaller than  $\text{LiCoO}_2$  ( $5.05 \text{ g/cm}^3$ ). 110 has a density of approx.  $4.6 \text{ g/cm}^3$ , 552 has approx.  $4.7 \text{ g/cm}^3$ . The same applies for "530" with a low density of  $4.4 \text{ g/cm}^3$ .

- Side reactions : Manganese and lithium rich cathode material (like "530") are not stable.  
25 They transform to an oxygen and lithium deficient cathode material at  $> 4.5\text{V}$  during first charge. After discharge a different material "530mod" is achieved. "530mod" is oxygen deficient and not thermodynamically stable. Even if the electrochemical properties of the resulting material are excellent, the transformation involves the release of oxygen, possibly

reacting with the electrolyte and forming undesired gas.

Important for real batteries is not only the gravimetric reversible capacity (mAh/g) but also the energy density (=capacity  $\times$  average voltage), here especially important is the volumetric energy density (Wh/L) of the electrodes. Essential to achieve a high volumetric energetic density of electrodes is (a) high powder density (b) a large capacity and (c) high voltage.

LiCoO<sub>2</sub> allows achieving powder densities of upto 3.5-4 g/cm<sup>3</sup>. This corresponds to approx. 70-80% of crystallographic density, or 20-30% porosity. Electrodes of complex layered materials or phosphates usually have a higher porosity, additionally the crystallographic density of the complex layered materials is 5-12% lower, the crystallographic density of LiFePO<sub>4</sub> is 30% lower. The same applies for spinel materials. This further reduces the energy density.

It is of immediate interest to achieve a cathode material which combines high volumetric and gravimetric energy density (like LiCoO<sub>2</sub> charged to  $\geq 4.4$ V) with high cycling stability and safety at low cost. Prior art does not disclose a fully satisfying solution for this problem. A better optimization can be achieved by applying the "non-uniform approach", disclosed in the actual invention. This approach utilizes the different performance requirements for small and large particles; in a preferred implementation it also utilizes the different performance requirements for inner bulk, outer bulk and surface of single particles.

Large dense particles have a long lithium diffusion path. Large particles contribute excessive to poor cycling stability if intercalation induced strain is involved. Large particles contribute excessive to poor rate performance if the lithium transport in the solid phase is slow. Small particles have a larger specific surface area. Small particles contribute excessive to low safety and poor cycling stability, if electrolyte reactions are involved.

If the cathode powder consist of small particles, then the preferred composition contains less cobalt and more of stable elements like manganese. The slower bulk lithium diffusion can be tolerated, what matters is the improved stability of the surface. If the cathode powder consist only of larger particles, the preferred composition contains more cobalt, and less

manganese because a fast bulk-lithium diffusion is required, whereas a slightly lower stability of the surface can be tolerated. Electrodes utilizing materials with very uniform particle size in principle have one preferred, optimized, uniform composition. This however is not feasible, and usually not preferred because the desired higher powder densities are achieved by more complex particle size distributions. In this case only the application of the "non-uniform" principle allows for fully optimization, resulting in a powder with size dependent composition.

A cathode which consists of particles with significant open porosity, has one preferred optimized uniform composition. This however is not feasible, and usually not preferred because the desired higher powder densities are achieved by denser, monolithic particles. In this case the application of the "non-uniform" principle allows for fully optimization. This approach takes into account the different requirements for inner bulk and outer bulk and surface. In a typical example the outer bulk has a preferred composition containing less cobalt than the inner bulk.

There are disclosures about mixtures of active cathodes materials (for example US 6,007,947 and US 6,379,842 (Polystor) "Mixed lithium manganese oxide and lithium nickel cobalt oxide positive electrodes"). There are also disclosures about powders being a mixture of  $\text{LiCoO}_2$  and spinel. These powder is obviously not uniform - particles of the different cathode components have different composition. These disclosures however are unrelated to the "non-uniform approach" of the actual invention. The described prior art does not differentiate between performance requirements for large and small particles, and it does not differentiate between requirements for inner bulk, outer bulk and surface of particles. Instead of this, rather the general "bulk" chemistry of the electrochemical cell is changed. Particularly, each cathode component itself is "uniform", the composition of large and small particles is the same, and the composition of inner bulk, outer bulk and surface is the same.

It can be summarized that conventional cathode materials are not fully optimized. Applying the "non-uniform principle" allows to achieve non-uniform cathode materials which are better optimized. This is because the performance requirements for large and small particles are different. Furthermore, uniform cathode materials are not fully optimized.

because the performance requirements for inner bulk, outer bulk and surface are different. Particularly, the requirements for chemical stability in contact with electrolyte, for the lithium diffusion constant, for the electronic conductivity and also for the morphology vary with particle size, and they also vary from the outer bulk to the inner bulk of a single particle.

5

#### Detailed description of invention

A very simple example (partially implementing the "non-uniform" principle) is a non-uniform cathode material being a mixture of at least two different cathode materials with different particle size distribution. One cathode component has large particles (for example  
10 having a distribution centered at  $\geq 20 \mu\text{m}$ ); its composition allows for fast bulk diffusion (for example  $\text{LiCoO}_2$  or "118". The other cathode component has small particles (for example having a distribution around  $5 \mu\text{m}$ ) and a composition, which ensures acceptable safety (for example "111" or "442").

A further reaching implementation of the "non-uniform" principle results in a more  
15 complex size-composition distribution. An example is a cathode material where large particles have a composition like  $\text{LiCoO}_2$  or "118", small particles have a composition like "442" and intermediary sized particles have an intermediary composition like "111", "112" etc. Such cathode materials are easily achieved by the method disclosed further below.

A still further application of the "non-uniform" principle results in a cathode material  
20 having a composition-size distribution, and additionally, particles have a different composition in the inner bulk and the outer bulk and surface. An example is a cathode material where large particles have a composition "118" in the outer bulk and a higher cobalt content in the inner bulk. Small particles have a composition "111" in the inner bulk and "552" in the outer bulk. Intermediary particles have an intermediary averaged composition,  
25 also richer in cobalt in the inner bulk. Such cathode materials can be achieved by the method disclosed further below.

A still further application of the "non-uniform" principle would result in a cathode material, where particles have a monolithic inner bulk, but the morphology of the outer bulk

near to the surface is structured. Such cathode materials can be achieved by the method disclosed further below.

Many further reaching applications of the "non-uniform" principle are possible, but not all can be achieved easily at low cost. Two examples: (1) The porosity of electrodes preferable decreases from the surface towards the current collector, this would allow for faster rates at the same averaged porosity. (2) Safety requirements in the center of a battery are more severe than at the outside (here the evolved heat is faster dissipated). A "non-uniform" improved battery would have a jelly roll, where the (averaged) composition and morphology of the cathode powder would changes from the outside to the inside. The actual invention does not disclose methods how to achieve these and other possible further implementations of the "non-uniform" principle.

The actual invention discloses cathode materials which a size depended composition, which allows to solve or improve many of the before mentioned problems. In a special implementation large particles have a composition near to  $\text{LiCoO}_2$  (for example "118") allowing for a high Li diffusion constant, thus a sufficient rate performance is achieved. The large particles contribute only a small fraction to the total surface area of the cathode. Therefore the quantity of heat evolving from reactions with electrolyte at the surface or in the outer bulk is limited; as a result large particles contribute little to poor safety. Small particles have a composition with less cobalt to achieve an improved safety. The lower lithium diffusion constant can be tolerated in small particles without significant loss of rate performance because the solid state diffusion path length is small.

A powder with a size depended composition can be achieved by a process, which involves a precipitation reaction utilizing seed particles. The precipitation reaction is characterized that the transition metal composition of the precipitate differs significantly from the transition metal composition of the seed particles. The precipitate can additionally contain further metal cations, like Mg, Al etc. Typically a flow of dissolved mixed transition metal salt, and a flow containing a suitable counter-anion (like NaOH or  $\text{Na}_2\text{CO}_3$ ) are fed to an agitated reactor, which contains a slurry of dispersed seed particles. In a preferred

implementation,  $\text{LiCoO}_2$ , or  $\text{LiCoO}_2$  based materials are used as seed particles. Preferable, the particles are monolithic. Structured secondary particles (agglomerates of smaller primary particles) are less desired. After a successful precipitation, a uniform layer of precipitate with sufficient adhesion covers all seeds particles. The amount of the precipitated layer is significant, so that the averaged (transition) metal composition of the particles is significantly different from that of the seed particle. The thickness of the precipitated layer is uniform, in this way the average composition of small particles differs from the composition of large particles, yielding the desired size-composition distribution. Furthermore, it is preferred that the precipitate has a low porosity, and covers completely the seed. Basically no particles, not having a seed-particle core are present. To achieve this goal, it is important during precipitation to keep the degree of supersaturation low. Especially important is the choice of reaction conditions like flow rate, pH, temperature, volume, agitation, additives (like ammonia), content of oxygen, thickening, shape of reactor, etc.,

Instead of  $\text{LiCoO}_2$  other materials can be used as seed materials. Preferably, the seed itself has a high energy density, if it would be applied as cathode material. A possible example is modified  $\text{LiNiO}_2$  (like Al and/or Co doped  $\text{LiNiO}_2$ ). Alternatively, the seed can be a precursor (for example a transition metal oxide), which converts to a cathode with high energy density during the heat treatment.

After precipitation the slurry is washed and dried. Alternatively an equilibration in a salt solutions to remove unwanted ions by ion exchange is possible, followed by wash and dry. After adding of a controlled amount of a source of lithium (like  $\text{Li}_2\text{CO}_3$ ) and mixing, at least one heat treatment follows. During the heat treatment a chemical reaction proceeds. The precipitated layer reacts with lithium and preferable, a lithium transition metal phase with layered crystal structure phase is formed. During the heat treatment also a diffusion reaction between layer and seed occurs, which relaxes the transition metal compositional gradient. The sintering conditions are important since excessive sintering would cause a low surface area, and in some cases the "non-uniform" character would be lost. Not enough sintered samples can result in a too high porosity, and a too large surface area, and the gradient between outer

phase (originating from the precipitate) and inner phase (originating from the seeds) might be too steep. In a preferred implementation of the invention, after sintering the cathode powder consists of particles being lithium transition metal oxide with layered crystal structure (typical space group : r-3m).

5       The choice of suitable seeds, precipitation and sintering conditions allow to optimize the final cathode powder. The (averaged) composition of particles varies with particle size. Preferably, also the composition varies between inner bulk and outer bulk and surface. A preferable morphology can be achieved. Particularly the surface and the outer bulk near to the surface can be modified without altering the dense monolithic structure of the inner bulk. One  
10   preferred example is a smooth surface with low surface area. Another preferred example is a slightly structured surface with larger surface area. The first is desired if safety is of concern, the latter can be preferred if impedance layers are of concern. Many more morphologies can be achieved. Under certain conditions deep valleys or pin-wholes, penetrating straight into the bulk of the particle can be achieved. This might be desired if large particles with sufficient  
15   rate performance are of interest. During sintering, beneficial epitaxi-related effects between the outer phase and the inner phase can be desired.

      The disclosed method allows to obtain a non-uniform cathode material at lowered cost. In the following the cost of a non-uniform cathode is compared with  $\text{LiCoO}_2$ , low cobalt complex cathodes and high cobalt complex cathodes.  $\text{LiCoO}_2$  has a medium high price  
20   because the cobalt precursors are expensive, but the processing is reasonable cheap. Complex low-Co materials like "111", "442", "530" etc. usually have a medium to medium high price because the precursors are cheaper, but often the processing (co precipitation) is expensive. High Co complex cathodes like "118" are expensive. The precursors (cobalt) are expensive, and the processing (typically precipitation) is expensive as well. Compared to "118" the "non-  
25   uniform" cathode materials of this invention have similar or better performance, but can be prepared at lower cost.

In the following aspects of the invention are described by example

## Examples

**Example 1)** Preparation of a powder, having particles with size dependent composition

**Seed particles :** Commercial  $\text{LiCoO}_2$  with broad particle size distribution, consisting of monolithic particles (not secondary particles being agglomerates of primary particles) is used as seed material. Figure 1 shows an FESEM image of the applied powder.

**Precipitation :** 3 kg of  $\text{LiCoO}_2$  and 1.4 L  $\text{H}_2\text{O}$  are added to a 5 L reactor. A flow of 4M  $\text{NaOH}$  solution and a flow of 2M  $\text{MSO}_4$  solution ( $\text{M}=\text{Mn}_{1/2}\text{Ni}_{1/2}$  "110") are added to the reactor during rigid stirring. The temperature is kept at  $95^\circ\text{C}$ , the flow rates were controlled so that the pH is kept stable. After 70 minutes the precipitation is interrupted, clear  $\text{Na}_2\text{SO}_4$  solution is removed from the solution, and the precipitation is continued for another 70 minutes. A total of 0.25 mol  $\text{M}(\text{OH})_2$  is precipitated per 1 mol  $\text{LiCoO}_2$ . The resulting slurry is decanted, and equilibrated over night in 0.3 M  $\text{LiOH}$  solution, followed by wash and filtering. The filtercake is dried at  $180^\circ\text{C}$  in air. Figure 2 shows an FESEM image of the achieved powder.

**Reaction :** 3.5 g  $\text{Li}_2\text{CO}_3$  is added per 50 g of dried powder and mixed. A solid state reaction is performed at  $980^\circ\text{C}$  for 24 hours, after that the powder is grinded (very low impact) and sieved, resulting in a powder of high press density. Figure 3 shows an FESEM image of the achieved powder.

**Powder properties :** Powder density is measured by pressing pellets. At  $2000 \text{ kg/cm}^2$  a press density of  $3.4\text{--}3.5 \text{ g/cm}^3$  is achieved. The particle size distribution is bimodal, with centers at approx.  $20 \mu\text{m}$  and  $5 \mu\text{m}$ . Large particles have a composition of  $\text{LiCo}_{1-x_1}\text{M}_{x_1}\text{O}_2$ , small particles have a composition  $\text{LiCo}_{1-x_2}\text{M}_{x_2}\text{O}_2$  with  $\text{M}=\text{Mn}_{1/2}\text{Ni}_{1/2}$  and  $x_1 \approx 0.05$  and  $x_2 \approx 0.2$ . The composition can be checked by a suitable separation of large and small particles (for example by dispersing in a liquid), followed by ICP chemical analysis.

**Electrochemical properties :** Coin cells with Li anode are prepared. The reversible capacity (C/10 rate) is  $> 165 \text{ mAh/g}$ . The rate performance (discharge to 3.0V) is satisfying, the ratio of capacities at  $2\text{C} : \text{C}/5$  rate is  $> 93\%$ . Figure 4 shows the first cycle voltage profile and the rate performance discharge profiles. An excellent cycling stability is achieved at 4.4V. Figure

5 compares the initial discharge profile at C/10 rate and 1C rate (cycle 2 and 5) with the discharge profiles at the same rate after extended cycling (cycle 51 and 52). At least 98% of capacity has remained. Very little impedance built-up is observed. At this voltage  $\text{LiCoO}_2$  would not cycle stable. DSC of charged electrodes shows significant changes compared to bare  $\text{LiCoO}_2$ .

#### Example 2)

Structural analysis : EDS mapping, quantitative analysis of EDS spectra of large and small particles and Rietveld analysis of X-ray diffraction data of the cathode powder of example 1 shows that a  $\text{LiCoO}_2$  phase remains in the inside of larger particles, the outside being  $\text{LiCo}_{1-2x}\text{Mn}_x\text{Ni}_x\text{O}_2$  with  $x \approx 0.13 \dots 0.16$ , smaller particles are monophase with  $x > 0.16$ .

#### Comparative example 3:

The intention of this example is to demonstrate that the preparation of a cathode with particles having a size dependend composition is possible at low cost.

A typical precipitation reaction to produce complex cathode materials involves large liquid reactor volumes, large amounts of waste, and the loading of drying ovens, furnaces etc. is low. Example 1 described the preparation of 3.7 kg of a cathode material with an (approximate) averaged composition  $\text{LiCo}_{0.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$ . The preparation included a 2-step precipitation reaction using a 5 L reactor. The powder densities during processing were high (volumes were less than 1.5 L of powder (before adding  $\text{Li}_2\text{CO}_3$ ) and less than 2 L powder (after  $\text{Li}_2\text{CO}_3$  addition) ). Waste was about 10 L of  $\text{Na}_2\text{SO}_4$ .

For a comparison, the same equipment is used to prepare a uniform cathode material having the same composition  $\text{LiCo}_{0.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$  ("118"). The preparation is similar as described in example 1 with the following exceptions:

- (a) the transition metal flow was transition metal sulfate (2M) not having the "110" but the "118" composition
- (b) no seed particles were applied

(c) after precipitation 0.53 mol  $\text{Li}_2\text{CO}_3$  were added per 1 mol of the mixed transition metal hydroxide

0.8 kg of final material was achieved. The powder densities during processing were low. The total involved powder volumes (before the heat treatment) exceeded the volumes of example

- 5 1. The same total amount of waste was produced. Summarizing: The cost of processing was the same as in example 1 but only 20% of the total mass was achieved.

#### Example 4)

A  $\text{LiCoO}_2$  powder, the powder containing a significant amount of large ( $\approx 20 \mu\text{m}$ ) and smaller  
10 particles (size 3-10  $\mu\text{m}$ ) is used as seed. The small particles have approx. 50% of the mass and they dominantly contribute to the surface area of the cathode.

A cathode material is prepared similar as described in example 1 with the following exception:

- (a) only 2 kg seeds are used  
15 (b) 0.4 mol transition metal hydroxide is precipitated per 1 mol of  $\text{LiCoO}_2$   
(c) the transition metal sulfate flow contained is not "110" but "331"  
(d) the amount of  $\text{Li}_2\text{CO}_3$  is adjusted (0.53 mols Li per 1 mol precipitate)

As a result a cathode powder is achieved where large particles have an outer and inner phase.

The inner phase has a composition near to  $\text{LiCoO}_2$ . The outer phase is basically  $\text{LiCo}_{1-2x}\text{Mn}_x\text{Ni}_x\text{O}_2$  with  $x \approx 0.13 \dots 0.16$ . Smaller particles are monophasic with  $x > 0.16$ . Small particles  
20 have a composition with  $x > 0.5$ .

#### Example 5)

Instead of  $\text{LiCoO}_2$   $\text{LiCo}_{0.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$  is used a seeds

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#### Example 6)

Instead of a "110" precipitate a manganese rich precipitate (like "530") is chosen.

Example 7)

The sintering temperature was lowered to about 900°C , much less than 980°C. A cathode material with a structured surface, having an increased surface area is achieved.

5 Example 8)

The sintering temperature was increased to 1020°C , much more than 980°C. A cathode material with a low surface area is achieved. Now a cathode particles with size dependent composition are achieved. Small and medium sized particles are one-phase, having the same composition in the outer and inner bulk.

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Example 9)

The coprecipitation reaction is modified so that additionally a thin "coating" layer is achieved. Typically, at the end of the precipitation, only for a limited time, soluble salts, or pigments of inactive elements are added to the reactor. Typical elements are Al, Mg, Ti, Zr, Sn etc.

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Example 10)

The coprecipitation reaction is modified. As seeds a  $\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$  based cathode is used. The precipitate contains at least 70% cobalt. After heat treatment a cathode is achieved which has a size depending composition. If a cheap  $\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$  is available, the resulting  $\text{Li}_x\text{M}_{1-x}\text{O}_2$  ( $\text{M}=(\text{Mn}_{1/2}\text{Ni}_{1/2})_{1-z}\text{Co}_z$  ,  $z < 0.5$ ) has a lower cost than a bulk material with the same average composition prepared from mixed precipitated hydroxide. The precipitation can further be modified to involve inert metal cations like Al, Mg, Zr, Ca, Ti, Zn, Sn etc, which preferable are inserted to the outermost region of the precipitate.

20

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### Claims

1. A powdery electrode material, with "non-uniform" composition characterized that particles have a distribution of compositions, the composition depending on the size of particles
- 5 2. A non-uniform positive electrode material according claim 1
3. A powdery material according claim 1 or 2 having not a narrow particle size distribution
  - where the composition of single particles varies with the size of the single particle
  - a narrow distribution defined by  $d_{90} / d_{10} < 2$
- 10 4. A powdery cathode material having not a narrow particle size distribution
  - where the composition of single particles varies with the size of the single particle
  - a narrow distribution defined by  $d_{90} / d_{10} < 2$
5. A powdery cathode material basically being lithium transition metal oxide having not a narrow particle size distribution
- 15
  - the transition metal consist to at least 90% of Mn, Co and Ni
  - where the composition of single particles varies with the size of the single particle
  - a narrow distribution defined by  $d_{90} / d_{10} < 2$
6. A powdery cathode material according claim 5 having a layered crystal structure
7. A powdery cathode material according claim 5 or 6 further characterized that the total
- 20 transition metal contains
  - at least 5% manganese and
  - at least 65% of another transition metal chosen from Co and/or Ni
8. A powdery cathode material according claim 7 characterized that the total transition metal contains at least 5% manganese and at least 70% cobalt
- 25 9. A powdery cathode material basically being lithium transition metal oxide having not a narrow particle size distribution
  - where the composition of single particles varies with the size of the single particle
  - large particles have a composition  $Li_xMO_2$  where M to at least 65% is cobalt or nickel

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- small particles have a composition  $\text{Li}_x\text{M}'\text{O}_2$  where  $\text{M}'$  contains less cobalt and more manganese than M.

- basically all bulk of all particles has a layered crystal structure

- a narrow distribution defined by  $d_{90} / d_{10} < 2$

5 10. A powderous cathode material according claim 9 furthermore being characterized that the inner bulk of larger particles has a composition  $\text{Li}_x\text{MO}_2$  where M to at least 80% is cobalt or nickel.

11. A powderous cathode material according claim 10 where M to at least 80% is cobalt

10 12. A powderous electrode material according to one of the claims 1-11 furthermore being characterized that it consists of single particles which have a Co content continuously decreasing with particle size

13. A powderous electrode material according claim 12 furthermore being characterized that the single particles contain manganese, where the manganese content continuously decreases with particle size

15 14. A powderous electrode material according claim 13 furthermore being characterized that the single particles contain manganese, where the manganese content continuously decreases with particle size, the manganese content roughly being proportional to the inverse of the radius.

20 15. A powderous electrode material according to one of the claims 12-14 furthermore characterized that the outer bulk of basically all larger particles contains less cobalt than the inner bulk.

16. A method to prepare the electrode material of one of the claims 1-15 involving a precipitation reaction, the precipitation reaction being characterized that

- a transition metal containing precipitate is precipitated onto seed particles

25 - the transition metal composition of the seed particles differs significantly from that of the precipitate

- basically all obtained particles contain a core, originating from a seed, completely covered by a layer of precipitate

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17. A method according claim 16 furthermore characterized that
- the precipitate contains manganese
  - the seeds dominantly are monolithic particles chosen from  $\text{LiCoO}_2$  or  $\text{Li}_x\text{MO}_2$  where M contains at least 75% Co or Ni)
- 5 18. A method according claim 17 furthermore characterized that at least 40% of the transition metal of the precipitate is manganese
19. A method according one of the claims 16-18 furthermore characterized that the outer layer of the resulting precipitate contains further metal elements, preferable chosen from Al, Mg, Ti, Zr, Sn, Ca, Zn
- 10 20. A method according one of the claims 16-19 involving a mixing of the composite (seed+precipitate) powder with a source of lithium, followed by a heat treatment
21. The method of claim 20 where the heat treatment is made in air, the temperature being within the range from 750 to 1050°C
22. The method of claim 21, the temperature being in-between 850-950°C
- 15 23. A electrochemical cell containing a cathode material according one of the claims 1-15, or a cathode material prepared by the method described in 16-22

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Figure 1)  $\text{LiCoO}_2$  seed particles

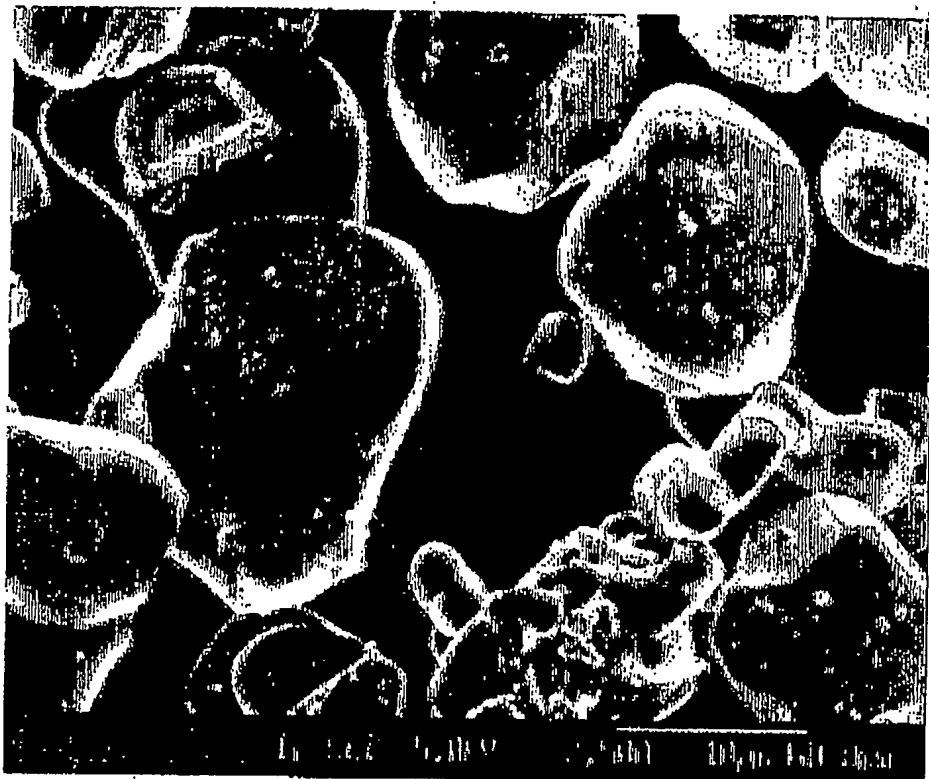
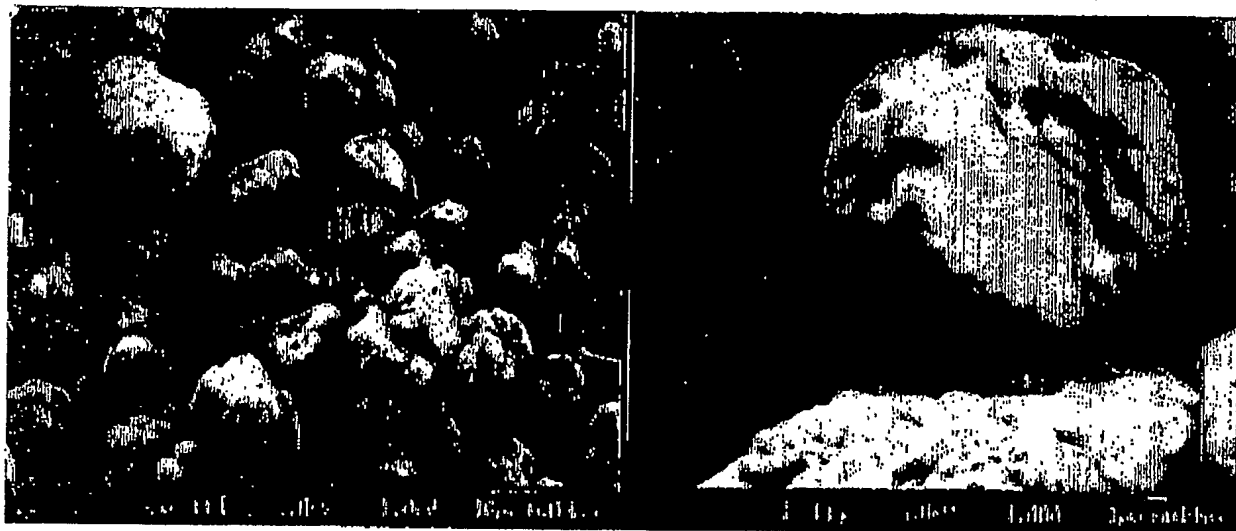


Figure 2)  $\text{LiCoO}_2$  covered with  $\text{Mn}_{1/2}\text{Ni}_{1/2}$  mixed hydroxide.



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Figure 3) The cathode of example 1 after sintering



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Figure 4) First cycle profile and rate performance of the cathode of example 1

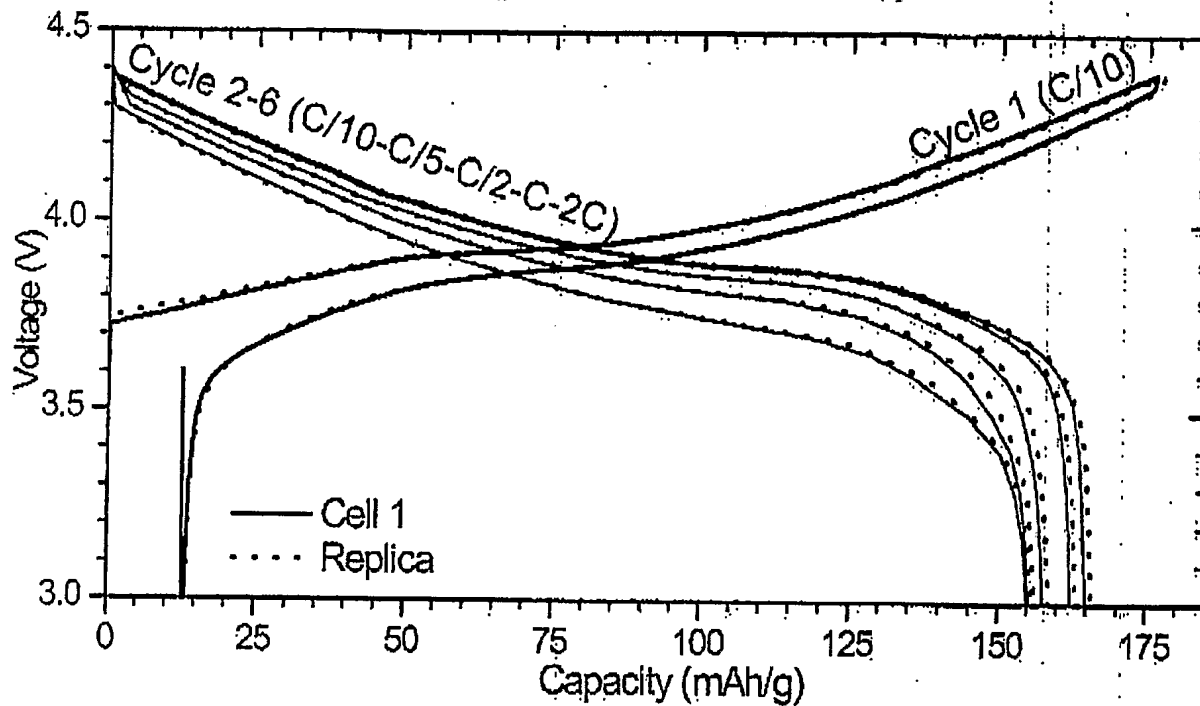


Figure 5) Cycling stability of the cathode of example 1

